Photocatalytic Methanol Reforming on Au/TiO_2 for Hydrogen Production

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Abstract

Methanol can be reformed with water, at ambient temperature, using photocatalysis, and this reaction represents a possible low energy, more sustainable pathway to hydrogen production than (for instance) steam reforming. The requirements for the catalysts are rather strict since titania itself is almost inactive for anaerobic photocatalysis, whereas the addition of a very limited range of metals to the surface renders it active. Surprisingly, this includes gold, which shows one of the highest reactivities for hydrogen production. The mechanism is proposed to involve the methoxy and formate intermediates, the latter being implicated in the route to CO_2 and hydrogen production. One oxygen atom is supplied from the titania support, which is replaced in the catalytic cycle by oxygen from water. The threshold for the excitation is that for bandgap excitation into the titania conduction band, which stores the energy for reactivation, and this is mediated by electrophilic oxygen.

Introduction

Several metals in the form of nanoparticles loaded on metal oxides exhibit activity for photocatalytic production of hydrogen from water (1-4). Among them, gold has received attention recently in pollution control and fuel cell applications (5,6), but has received very little attention with regard to photocatalysis.

The activity of gold loaded on metal oxides depends on many factors such the type of support material, the preparation method and the calcination temperature. This group has carried out a number of investigations concerning the activity of Pd/TiO_2 (7-13) and Au/TiO_2 to produce hydrogen gas (11-14). We have found that Au/TiO_2 was slightly more reactive than Pd/TiO_2 and mixed metal catalysts of gold and palladium on titania have greater activity than sums of the reaction using the single metal catalysts (14).

In this paper, we show the activity of Au/TiO_2 in the liquid phase and, for the first time, in the gas phase, and a mechanism for the photocatalytic reforming of methanol is presented.

Experimental

Experiments were carried out in a Pyrex reaction flask which contains two arms, one for purging the reaction by argon and the other for sampling through a rubber septum. For liquid phase reactions, the reaction mixture is 0.2 g of the catalyst, 100 ml of deionized water and 100 μl methanol. Note that we have previously found that the reaction is close to zero order in the concentration of methanol in solution (7,8). For gas phase reactions, 0.05 g of the catalyst was mounted on a slide which is supported in a modified reactor without direct contact with the reaction mixture (15 ml of deionized water and 100 μl methanol). There is no forced circulation of the gas phase.

In both cases, the mixture was stirred with a magnetic stirrer and was illuminated with light from a 400 W xenon arc lamp (Oriel model) from the side. Every 30 minutes, 0.2 ml samples were taken from the gas phase and analysed by GC (Varian 3900).

The catalyst was prepared by the incipient wetness method as follows. The appropriate mass of metal salt ($HAuCl_4$) was dissolved in water and a volume of this solution was added to P25 titania (Degussa) which was just sufficient to fill the pores of the support. The sample was then dried in an oven at 110°C for 2 h, ground in a pestle and mortar, calcined at 500°C for 2 h and finally sieved to less than 53 μm aggregate size.

Results and discussion

a) Liquid phase

It was found that the gold was active for photocatalysis, as shown in Figure 1, and had very good activity compared with

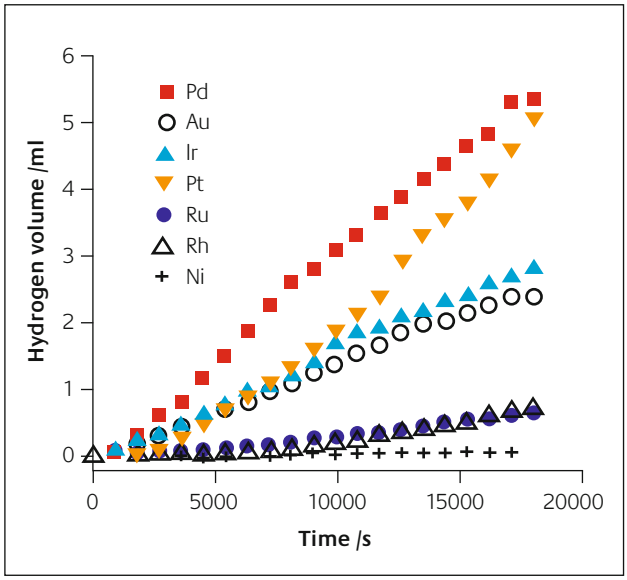

Figure 1
Hydrogen production from titania loaded with various metals

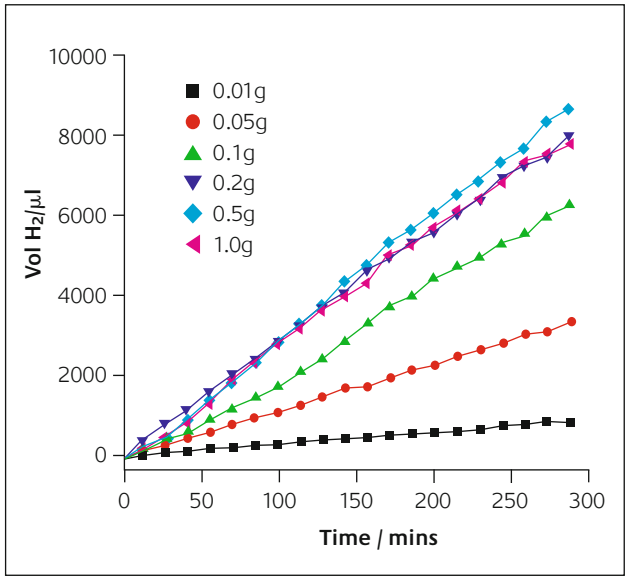

Figure 2
The effect of varying the loading of catalyst on the slide upon hydrogen production from Au/ TiO_2 for gas phase reforming of methanol

other metals. Indeed, when considered on a molar metal basis it is the most active metal, except for Pt. The rate of hydrogen production was ~40 µl/g catalyst/min. Note that control experiments showed that no hydrogen was produced from the catalysts if no light was admitted to the sample, while only 5 µl/g catalyst/min were produced in the absence of methanol, and only 3 µl/g catalyst/min were produced for the full reaction mixture on P25 titania alone (no metal).

It can be seen that it is the most noble metals that are the most active for the reaction, whereas others (Ru, Rh) are much less active, with Ni showing little evidence of any activity at all. It is likely that this is associated with the reducibility of the metal (for example, the heat of formation of NiO is -244 kJ mol^{-1}, whereas that of PdO is only -85 kJ mol^{-1}), and that Au, Pd and Pt are readily reduced in the reaction mixture and in the presence of light.

b) Gas phase photocatalysis

Up to this point all of our work was with the catalysts present in the liquid phase with the reactants, so we have now explored how efficient the reaction may be, if it proceeds at all, in the gas phase. For this work, the catalyst was mounted on a slide as a thin layer, and this situation allows for all of the catalyst particles in the sample to be directly illuminated.

As shown in Figure 2, 0.2 g of 2% Au/TiO_2 produced 8000 µl in 5 hours, a rate of about 135 µl/g catalyst/min. Thus the rate in the gas phase was much more than of that in the liquid phase. At least one reason for this improvement is that the light is focused better on the catalysts, since they are much more localised in space, while in the liquid experiment they are much more dispersed, and some particles do not receive the light directly at all. In experiments varying the loading of catalyst on the slide it is evident that the maximum rate is obtained at about 0.2 g loading, and this means that little light is transmitted through the slide. Thus at higher loadings the catalyst closest to the slide is shadowed by that above it, closest to the light source.

The mechanism of photocatalytic methanol-water reforming

We have previously proposed a mechanism for the reforming of methanol photocatalytically on Pd/TiO_2 catalysts (7-13). The most important part of this was that methanol dehydrogenation occurred on the Pd, even in the absence of light, but the reaction stopped because the metal surface became blocked with CO, which is strongly adsorbed on Pd. The role of light was to create an active state of oxygen (probably O^-) by absorption of light by band-gap excitation in the titania. Although Debeila et al. (15). have reported that the bandgap of titania can be reduced by gold, we found the threshold for photocatalysis to be ~3.2 eV, as expected for unaffected titania. In turn then, this oxygen was capable of reacting with the poisoning CO to give CO_2, and maintained a steady state conversion of methanol. The oxygen vacancy in the titania lattice was filled by water reduction to produce hydrogen.

It is likely that the mechanism in the case of Au/TiO_2 is different from that on Pd/TiO_2. CO is bound much more weakly to the Au surface due to the low energy of d orbitals in Au. Thus the blocking surface intermediate from methanol is probably different from that with Pd. The candidate species could be methoxy or formate. We have evidence from TPD (Figure 3) that formate is the intermediate with Au/TiO_2, at least in an oxidising environment, leading to the CO_2/hydrogen coincident desorption from the surface at ~200°C, a feature which is not present for titania alone. Boccuzzi et al. have identified both intermediates to be present on Au/TiO_2 catalysts by infra-red (6). Whether it is the methoxy or the formate which is the pivotal intermediate, we believe that this intermediate is destabilised in the

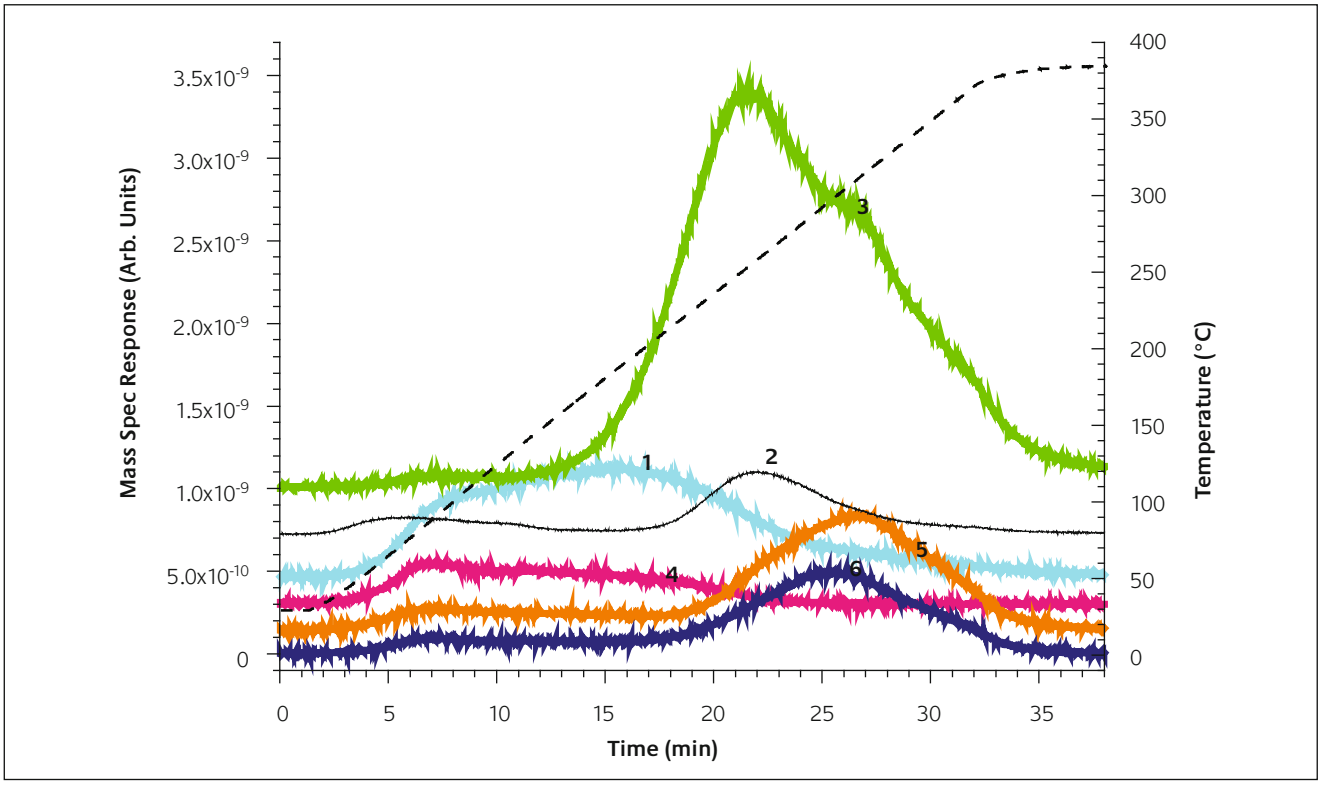

Figure 3

TPD after dosing methanol onto an oxidised Au/TiO_2 catalyst. Note the coincident desorption of H_2 and CO_2 at ~200°C indicative of formate formation. The methane and CO desorption is a characteristic of the titania support. Curve 1 is water (18 amu), 2 is CO_2 (44 amu), 3 is hydrogen (2 amu), 4 is methanol (31 amu), 5 is CO (28 amu) and 6 is methane (15 amu and there is coincident 16 amu)

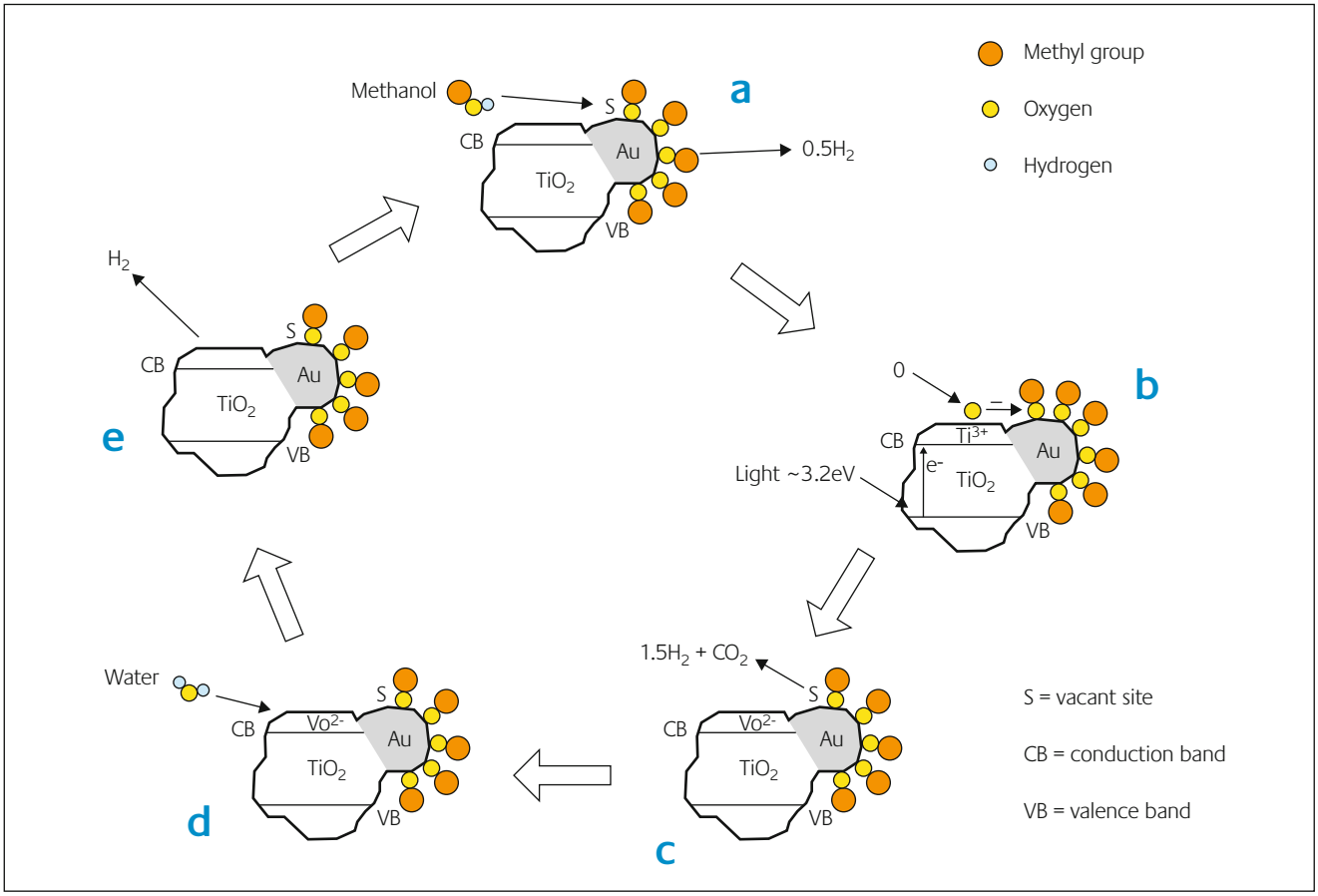

Figure 4

The proposed mechanism of anaerobic photocatalytic reforming of methanol on Au/TiO_2. Here we show the methoxy as the pivotal intermediate in the reaction, though it could be the formate

presence of light, again possibly by reaction with excited species from the support. Note that there are also methoxy intermediates on the titania support, as seen in Figure 3 and identified by infra-red (6), but these are more stable than those on the gold, produce different products (methane, CO and water), and appear to be unaffected by the presence of gold nanoparticles. Thus these are probably spectators during the course of photocatalysis, since no such products are evolved for titania alone.

It is possible to summarize the mechanism as depicted in Figure 4, showing the methoxy as the blocking species:

a) $CH_3OH + S \rightarrow CH_3O_a + 1/2H_2$

b) $Ti^{4+} O^{2-} + h\nu \rightarrow Ti^{3+} + O^-$

c) $CH_3O_a + O^- \rightarrow CO_2 + 1.5\ H_2 + S + V_O^-$

d) and e) $H_2O + V_O^- + Ti^{3+} \rightarrow O^{2-} + H_2 + Ti^{4+}$

here S is a free metal site, whereas V_o is an anion vacancy at the surface of the oxide

The reaction steps are shown schematically in Figure 4. In part a) methanol adsorbs at free sites on the gold and forms the methoxy intermediate which is stable in the absence of light and blocks the reaction. In b) light causes band gap excitation and reactive oxygen production which electrophilically attacks the methoxy to ultimately produce CO_2 and H_2 (c). In d) and e) water is shown oxidising the oxygen vacancy site yielding more hydrogen and completing the methanol-water reforming reaction.

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Michael Bowker is Director of the Wolfson Nanoscience Laboratory in the School of Chemistry at Cardiff University and heads the Heterogeneous Catalysis and Surface Science Group. His research group works in the fields of nanoscience, surface science and catalysis. He previously worked in academic and industrial positions. Philip Davies is a Senior Lecturer and is mainly involved in surface science research. Jane Greaves carried out a PhD in photocatalysis at Reading University with MB, and is now at the Open University. Layla Saeed Al-Mazroai is a second year PhD student at Cardiff working on aspects of photocatalytic water splitting as is Abdullahi Nuhu who is working on selective oxidation catalysis using gold.

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References

1 T. Kawai and T. Sakata, *Nature*, 1980, **286**, 474

2 T. Sakata and T. Kawai, *Chem. Phys. Lett.*, 1981, **80**, 341

3 K. Karakitsou and X. Verykios, *J. Catal.*, 1992, **134**, 629

4 C.E. Taylor R.P. Noceti, J.R. D'Este et al. *Studies in Surf. Sci. and Catal.*, 1996, **101**, 407

5 G.R. Bamwenda, S. Tsubota, T. Nakamura and M. Haruta, *J. Photochem. and Photobio. A: Chemistry*, 1995, **89**, 177

6 F. Boccuzzi, A. Chiorino and M. Manzoli *J. Power Sources*, 2003, **118**, 304

7 A. Dickinson D. James, N. Perkins, T. Cassidy and M. Bowker, *J. Mol. Cat. A*, 1999, **146**, 211

8 A.J. Dickinson, PhD Thesis, The University of Reading, 1997

9 L. Millard M. Bowker, *J. Photochem. Photobiol.*, 2002, **148**, 91

10 M. Bowker, D. James, P. Stone, R. Bennett, N. Perkins, L. Millard, J. Greaves and A. Dickinson, *J. Catal.*, 2003, **217**, 427

11 M. Bowker, L. Millard, J. Greaves, D. James and J. Soares, *Gold Bull.*, 2004, **37**, 170

12 L.R. Millard, PhD thesis, The University of Reading, 2003

13 D.W. James, M. Sc. thesis,The University of Reading, 1998

14 J. Greaves, PhD thesis, The University of Reading, 2005

15 M. Debeila, R. Mpfunzeni, E. Mokoena, M. Avalos, V. Petranovskii, N. Coville and M. Scurrell, *Mat. Sci. Eng.*, 2005, **A396**, 70